Claims

Claims 1-93. (cancelled)

- 94. (currently amended) A kinetic resolution process, comprising the step of reacting a silyl azide and a mixture of stereoisomers of a chiral cyclic substrate in the presence of a non-racemic chiral catalyst to produce by kinetic resolution a stereoisomerically enriched cyclic substrate or a stereoisomerically enriched azide-substituted product or both, wherein said chiral cyclic substrate comprises a carbocycle or heterocycle having a reactive center susceptible to nucleophilic attack by said silyl azide, and said non-racemic chiral catalyst comprises an asymmetric tetradentate ligand complexed with a metal atom, which complex has a rectangular planar or rectangular pyramidal geometry.
- 95. (previously presented) The process of claim 94, wherein said silyl azide is a trialkylsilyl azide.
- 96. (previously presented) The process of claim 94, wherein said silyl azide is trimethylsilyl azide.
- 97. (previously presented) The process of claim 94, wherein the metal atom is a transition metal from Groups 3-12 or from the lanthanide series.
- 98. (previously presented) The process of claim 94, wherein the metal atom is selected from the group consisting of Co, Rh, and Ir.
- 99. (previously presented) The process of claim 94, wherein the metal atom is Co.
- 100. (previously presented) The process of claim 94, wherein the non-racemic chiral catalyst is selected from the group consisting of chiral crown ethers complexed with a transition metal atom; the chiral catalyst represented by 102,

$$X_1$$
 X_2
 X_1
 X_2
 X_1
 X_2
 X_1
 X_2
 X_3
 X_4
 X_4
 X_4
 X_4
 X_4
 X_4
 X_4
 X_4
 X_4
 X_4

in which

the substituents R₁, R₂, Y₁, Y₂, X₁, X₂, X₃ and X₄ each, independently, represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol, amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH₂)_m-R₇,

or any two or more of the substituents taken together form a carbocycle or heterocycle having from 4 to 8 atoms in the ring structure, which ring structure may be a fused ring, as in the case of, for example, X_1 and X_2 forming a ring, or which ring may be a bridging ring, as in the case of R_1 and R_2 , X_2 and X_4 , or Y_1 and X_2 representing different ends of a single substituent,

with the proviso that at least one of R_1 , Y_1 , X_1 and X_2 is covalently bonded to at least one of R_2 , Y_2 , X_3 and X_4 to provide the β -iminocarbonyls as a tetradentate ligand;

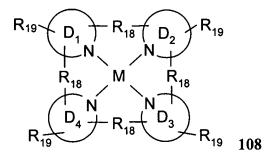
R₇ represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle; m is zero or an integer in the range of 1 to 8;

M represents a transition metal;

A represents a counterion or a nucleophile; and

the catalyst is asymmetric;

the chiral catalyst represented by 108,



in which

D₁, D₂, D₃ and D₄ each represent heterocycles, such as pyrrole, pyrrolidine, pyridine, piperidine, imidazole, pyrazine, or the like;

each R₁₈ occurring in the structure represents a bridging substituent which links adjacent heterocycles, and preferably contains at least one stereogenic center of the ligand. For example, each R₁₈, represents an alkyl, an alkenyl, an alkynyl, or -R₁₅-R₁₆-R₁₇-, wherein R₁₅ and R₁₇ each independently are absent or represent an alkyl, an alkenyl, or an alkynyl, and R₁₆ is absent or represents an amine, an imine, an amide, a phosphonate, a phosphine, a carbonyl, a carboxyl, a silyl, an oxygen, a sulfonyl, a sulfer, a selenium, or an ester;

each R₁₉, independently, is absent or represents one or more substituents of the heterocycle to which it is attached, each substituent independently selected from the group consisting of halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, and -(CH₂)_m-R₇;

or any two or more of the R₁₈ and R₁₉ substituents are covalently linked to form a bridge substitution;

R7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle;

m is zero or an integer in the range of 1 to 8;

M represents a transition metal; and

the catalyst is asymmetric;

the chiral catalyst represented by 112,

$$\begin{array}{c}
R_1 \\
R_2 \\
R_5 \\
R_4 \\
R_{11} \\
R_{12}
\end{array}$$

$$\begin{array}{c}
R_3 \\
R_4 \\
R_{13} \\
R_{14}
\end{array}$$

in which

each of the substituents R₁, R₂, R₃, R₄, R₅, R₁₁, R₁₂, R₁₃ and R₁₄, independently, represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro,

thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH₂)_m-R₇;

or any two or more of the substituents taken together form a carbocycle or heterocycle having at least 4 atoms in the ring structure;

R7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle;

m is zero or an integer in the range of 1 to 8; and

M represents a transition metal;

if R₅ is absent, at least one of R₁ and R₂ is covalently bonded to at least one of R₃ and R₄; and the catalyst is asymmetric;

the chiral catalyst represented by 114 and a complexed transition metal atom,

$$R_{21}$$

$$R_{22}$$

$$R_{24}$$

$$R_{23}$$

$$R_{23}$$

$$R_{24}$$

wherein

R₂₁ and R₂₂ each represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH₂)_m-R₇;

R₂₀ is absent or represents one or more substituents of the pyridine to which it is attached, each substituent independently selected from the group consisting of halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH₂)_m-R₇;

R₂₃ and R₂₄ each independently are absent or represent one or more substituents of the 1,3-diiminopropyl to which they are attached, each substituent independently selected from the group consisting of halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH₂)_m-R₇;

or any two or more of the R₂₀, R₂₁, R₂₂, R₂₃ and R₂₄ substituents are covalently linked to form a bridging substituent;

R₇ represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is zero or an integer in the range of 1 to 8; and the ligand is asymmetric; and

the chiral catalyst represented by 116 and a complexed transition metal atom,

$$Q_{8}$$
 Q_{8}
 Q_{8}

in which

each of the substituents Q₈ independently, are absent or represent hydrogen or a lower alkyl; each of R₂₅, R₂₆, R₂₇ and R₂₈, independently, represent one or more substituents on the ethyl or propyl diimine to which they are attached, which substituents are selected from the group of hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol, amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, and -(CH₂)_m-R₇; or any two or more of the substituents taken together form a bridging substituent;

R₇ represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle; m is zero or an integer in the range of 1 to 8; and the ligand is asymmetric.

101. (previously presented) The process of claim 94, wherein the non-racemic chiral catalyst is represented by structure A or its enantiomer:

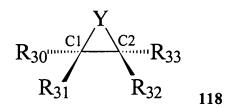
A

wherein

M represents Co or $Co(O_2CR)$; and

R represents alkyl or aryl.

- 102. (previously presented) The process of claim 101, wherein said silyl azide is a trialkylsilyl azide.
- 103. (previously presented) The process of claim 101, wherein said silyl azide is trimethylsilyl azide.
- 104. (previously presented) The process of claim 94, wherein the tetradentate ligand has at least one Schiff base that complexes with the metal atom.
- 105. (previously presented) The process of claim 94, wherein the chiral catalyst has a molecular weight of less than 10,000 a.m.u.
- 106. (currently amended) The process of claim 94, wherein the chiral cyclic substrate is represented by the general formula 118:



in which

Y represents O, S, $N(R_{50})$, $C(R_{52})(R_{54})$, or has the formula A-B-C; wherein R_{50} represents a hydrogen, an alkyl, a carbonyl-substituted alkyl, a carbonyl-substituted aryl, or a sulfonate, R_{52} and R_{54} each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C_1 - C_5 alkyl, O, S, carbonyl, or $N(R_{50})$; and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R₃₀, R₃₁, R₃₂, and R₃₃ represent organic or inorganic substituent which form a covalent bond with the C1 or C2 carbon atoms of **118**, and which permit formation of a stable ring structure including Y.

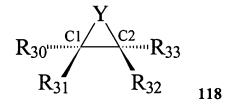
107. (**previously presented**) The process of claim 106, wherein the substituents R₃₀, R₃₁, R₃₂, and R₃₃ each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH₂)_m-R₇;

or any two or more of the substituents R₃₀, R₃₁, R₃₂, and R₃₃ taken together form a carbocylic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R₇ represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is zero or an integer in the range of 1 to 8.

108. (currently amended) The process of claim 94, wherein the <u>chiral cyclic</u> cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones and sultones.

- 109. (currently amended) The process of claim 94, wherein the chiral cyclic substrate is an epoxide.
- 110. (currently amended) The process of claim 94, wherein the chiral cyclic substrate is a terminal epoxide.
- 111. (previously presented) The process of claim 94, wherein the non-racemic chiral catalyst is immobilized on an insoluble matrix.
- 112. (previously presented) The process of claim 94, wherein the cyclic substrate is immobilized on an insoluble matrix.
- 113. (currently amended) A kinetic resolution process, comprising the step of reacting a silyl azide and a mixture of stereoisomers of a chiral cyclic substrate in the presence of a non-racemic chiral catalyst to produce by kinetic resolution a stereoisomerically enriched cyclic substrate or a stereoisomerically enriched azide-substituted product or both, wherein said chiral cyclic substrate comprises a carbocycle or heterocycle having a reactive center susceptible to nucleophilic attack by said silyl azide, and said non-racemic chiral catalyst comprises an asymmetric tridentate ligand complexed with a metal atom, which complex has a trigonal planar or trigonal pyramidal geometry.
- 114. (previously presented) The process of claim 113, wherein said silyl azide is a trialkylsilyl azide.
- 115. (previously presented) The process of claim 113, wherein said silyl azide is trimethylsilyl azide.
- 116. (previously presented) The process of claim 113, wherein the metal atom is a transition metal from Groups 3-12 or from the lanthanide series.
- 117. (currently amended) The process of claim 113, wherein the metal <u>atom</u> is selected from the group consisting of Co, Rh, and Ir.
- 118. (previously presented) The process of claim 113, wherein the metal atom is Co.
- 119. (previously presented) The process of claim 113, wherein the tridentate ligand has at least one Schiff base that complexes with the metal atom.

- 120. (currently amended) The process of claim 113, wherein the <u>non-racemic chiral</u> catalyst has a molecular weight of less than 10,000 a.m.u.
- 121. (currently amended) The process of claim 113, wherein the <u>chiral cyclic</u> substrate is represented by the general formula:



in which

Y represents O, S, $N(R_{50})$, $C(R_{52})(R_{54})$, or has the formula A-B-C; wherein R_{50} represents a hydrogen, an alkyl, a carbonyl-substituted alkyl, a carbonyl-substituted aryl, or a sulfonate, R_{52} and R_{54} each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C_1 - C_5 alkyl, O, S, carbonyl, or $N(R_{50})$; and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R₃₀, R₃₁, R₃₂, and R₃₃ represent organic or inorganic substituent which form a covalent bond with the C1 or C2 carbon atoms of 118, and which permit formation of a stable ring structure including Y.

122. (**previously presented**) The process of claim 121, wherein the substituents R₃₀, R₃₁, R₃₂, and R₃₃ each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -(CH₂)_m-R₇;

or any two or more of the substituents R₃₀, R₃₁, R₃₂, and R₃₃ taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure;

R7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and

m is zero or an integer in the range of 1 to 8.

- 123. (currently amended) The process of claim 113, wherein the <u>chiral</u> cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones, and sultones.
- 124. (currently amended) The process of claim 113, wherein the chiral cyclic substrate is an epoxide.
- 125. (currently amended) The process of claim 113, wherein the chiral cyclic substrate is a terminal epoxide.
- 126. (previously presented) The process of claim 113, wherein the non-racemic chiral catalyst is immobilized on an insoluble matrix.
- 127. (currently amended) The process of claim 113, wherein the <u>chiral</u> cyclic substrate is immobilized on an insoluble matrix.
- 128. (currently amended) The process of any of claims 94-127, wherein said <u>chiral</u> cyclic substrate is racemic.